Anisotropic Local Stress and Particle Hopping in a Deeply Supercooled Liquid

Sarika Bhattacharyya and Biman Bagchi*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India 560 012

The origin of the microscopic motions that lead to stress relaxation in deeply supercooled liquid remains unclear. We show that in such a liquid the stress relaxation is locally anisotropic which can serve as the driving force for the hopping of the system on its free energy surface. However, not all hoppings are equally effective in relaxing the local stress, suggesting that diffusion can decouple from viscosity even at the local level. On the other hand, orientational relaxation is found to be always coupled to stress relaxation.

Dynamics of supercooled liquid show many fascinating properties, namely, the nonexponentiality in various relaxation functions of dynamical variables, such as the stress, density, composition, polarization, and orientation [1–5]. One often observes a very slow power law decay in the intermediate to long times [6]. Although these have drawn the attention of experimentalists and theoreticians and have been extensively studied, many aspects still remain ill-understood. It is believed that the nature of the microscopic motion undergoes a drastic change at a temperature T_B (a temperature substantially below the melting temperature, T_m). At the temperature T_B, the continuous hydrodynamic-type motion, which is prevalent at higher temperature, changes to discontinuous motion. It is also believed that T_B is close to the temperature where effects of the underlying free energy landscape on the dynamics are felt for the first time [1]. T_B is also found to be close to the mode coupling temperature, T_c. This change in the nature of the microscopic motion is believed to be the origin of the experimentally observed α-β bifurcation [7] and also the crossover between the rotational and the translational relaxation times [8].

Because of the complexity of the problem, computer simulations have played a key role in augmenting our understanding in this area. In particular, simulations allow one to directly look at the microscopic events. The computer simulation studies of the stress autocorrelation function in the supercooled liquid could successfully reproduce the power law behavior of the stress autocorrelation function (SAF) [3,4]. However, in the deeply supercooled liquid, one finds that, within the simulation time, the relaxation, after an initial decay (typically 10%–20%), becomes fully arrested. The microscopic origin of the subsequent decay is unclear. The computer simulation studies further show that the orientational and translational hopping of particles are the only modes present and, hence, the stress relaxation can happen only via hopping. However, since the relaxation time is much much longer (could be of the order of ms or sec), the computer simulation results (which can explore mostly up to the nanosecond regime and sometimes the microsecond regime) cannot include the effects

of these hoppings. Therefore, one cannot explore the relationship between hopping and the *total* stress relaxation.

The experiments, on the other hand, are successful in showing the decay of the SAF. However, except a recent work using single molecule spectroscopy [9], these experiments are macroscopic and do not provide enough information of the microscopic motions in the system.

Majumdar [10] had earlier discussed the importance of local relaxation modes (of wavelength less than the short range order) in giving rise to nonexponentiality in the stress relaxation function. This work discussed relaxation in terms of relaxation within small regions, surfaces, and also volumes, with progressive lengthening of time scales. However, in that analysis the basic mechanism of relaxation was still assumed to be continuous.

In this Letter, we demonstrate for the first time that, in the deeply supercooled liquid (where hopping is the only surviving large amplitude motion), there is a close relationship between the *local* stress and the orientational and translational hopping. The local SAF is anisotropic and is found to change drastically during the hopping, thus showing that the local stress and the hopping of a particle are intimately connected. The anisotropy in the local stress could be the driving force for hopping. As the free energy of the system can be expressed in terms of the position dependent stress in a generalized Ginzburg-Landau formulation [11], the change of the anisotropic stress due to hopping should be regarded as the driving force for the transitions of the system between different minima of the free energy surface. However, not all hoppings are effective in relaxing the stress.

Our solvent is represented by a binary Lennard-Jones (LJ) mixture, which has been extensively studied [1,12–14] and is known to be a good glass former, and our solute probes are prolate ellipsoids. Pressure is kept constant by Andersen's piston method [15] while, in the case of temperature, a damped oscillator method has been adopted which keeps temperature constant at each and every time step [16]. The piston mass involved here is $0.0027(m_A/\sigma_A^4)$ which is regarded as optimum [16,17]. The interaction between two ellipsoids with arbitrary

orientations is assumed to be given by the Gay-Berne (GB) potential [18],

$$U_{GB} = 4\epsilon(\hat{r}, \hat{u}_1, \hat{u}_2) \left[\left(\frac{\sigma_0}{r - \sigma(\hat{r}, \hat{u}_1, \hat{u}_2) + \sigma_0} \right)^{12} \right.$$
$$\left. - \left(\frac{\sigma_0}{r - \sigma(\hat{r}, \hat{u}_1, \hat{u}_2) + \sigma_0} \right)^{6} \right], \qquad (1)$$

where $\hat{u}_1, \hat{u}_2$ are the axial vectors of the ellipsoids 1 and 2. $\hat{r}$ is the vector along the intermolecular vector $r = r_2 - r_1$, where r_1 and r_2 denote the centers of mass of ellipsoids 1 and 2, respectively. $\sigma(\hat{r}, \hat{u}_1, \hat{u}_2)$ and $\epsilon(\hat{r}, \hat{u}_1, \hat{u}_2)$ are the orientation-dependent range and strength parameters, respectively. σ and ϵ depend on the aspect ratio κ. The minor axis of the ellipsoid is equal to the diameter of the larger solvent and the major axis is 3 times that of the minor axis. Finally, the interaction between a sphere and an ellipsoid is accounted for by a modified GB-LJ potential given below:

$$U_{Ei} = 4\epsilon_{Ei} \left[\left(\frac{\sigma(\theta)_{Ei}}{r} \right)^{12} - \left(\frac{\sigma(\theta)_{Ei}}{r} \right)^{6} \right], \qquad (2)$$

where E denotes the ellipsoids and i can be A or B. The expression for $\sigma(\theta)_{Ei}$ is available [19].

The ellipsoid in the binary mixture system with the above-mentioned potential is a well-behaved system, and it can also exhibit the experimentally observed anomalous viscosity dependence of the orientational correlation time [19]. Four ellipsoids were placed far from each other in a binary mixture of 500 particles with a number of A-type particles, $N_A = 400$, and a number of B-type particles, $N_B = 100$. The reduced temperature is expressed as $T^*(= k_B T/\epsilon_A)$, the reduced pressure as $P^*(= P\sigma_A^3/\epsilon_{AA})$, and the reduced density as $\rho^*(= \rho\sigma_A^3)$. The time is scaled by $\tau = \sqrt{(m_A \sigma_A^2/\epsilon_{AA})}$. The time step of the simulation is 0.002τ; the system is equilibrated for 1.5×10^5 steps and the data collection step is 5×10^6. The studies have been performed at $T^* = 0.8$ and the $P^* = 6$ and 10.

At $P^* = 6$, both hopping and continuous motions exist in the system, thus the stress relaxation could not be directly correlated with the hopping. At $P^* = 10$, only microscopic motion that survives is hopping. In a recent study, we have reported observation of correlated translational and orientational hopping [20] at this pressure. After extensive simulations, we could find only two different kinds of motions. The translational hopping was either associated with correlated hopping of 5–6 nearest neighbors or it exhibited a motion in a ringlike tunnel. While it is possible that other types of motion such as isolated hopping can exist, we could not find them. The hopping rate was found to be 2×10^7 where both types of motions occurred with almost equal frequency. In the following, we focus on the stress relaxation and its relation *vis-á-vis* hopping at $P^* = 10$ and $T^* = 0.8$. The reduced density of the system is 1.41.

In Fig. 1, we show two different kinds of spatial hopping observed in our simulations. Both hoppings are associated with orientational hopping. In the inset, we also plot the orientational time correlation functions (OCF), before, during, and after the hopping. Figure 1(a) shows the trajectory of the first tagged ellipsoid, and the inset shows its orientational time correlation function, $\langle P_2(\hat{u}_i(0)\hat{u}_i(t)) \rangle / \langle P_2(\hat{u}_i(0)\hat{u}_i(0)) \rangle$, where P_2 is the second order Legendre polynomial. The hopping takes place in 20τ and the displacement is 0.5σ. Here the ellipsoid hopping is accompanied by hopping of 5–6 of its nearest neighbors. The OCF decays only during the period of hopping. In Fig. 1(b), the trajectory of the second tagged ellipsoid and, in the inset, its orientational time correlation functions are shown. Note that in this case the displacement of the particle is large (1.1σ) and it also takes place over a very long period of time (50τ). Here we find that the tagged particle is moving in a ringlike tunnel. Although the orientational correlation function decays during
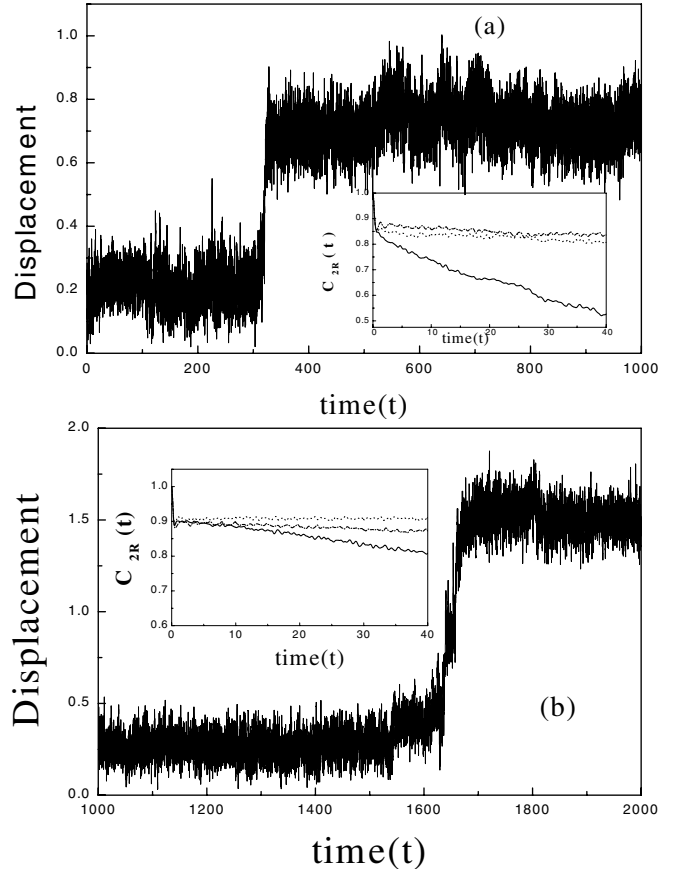

FIG. 1. (a) The displacement of the first tagged ellipsoid over 1000τ. There is a hopping of the ellipsoid around 300τ. In the inset, we plot the orientational correlation function obtained at different intervals. The solid line denotes the OCF calculated during hopping and the dotted and the dashed-dot lines denote the same before and after hopping, respectively. (b) Same as (a) but for the second tagged ellipsoid. The plots are at $P^* = 10$ and $T^* = 0.8$.

the hopping, its decay is less when compared to that of the first tagged particle.

The motions in a stringlike and a ringlike tunnel in a deeply supercooled liquid have been reported earlier by other authors, although they did not discuss these large displacements over a long time for the ringlike motion [21].

In the following, we discuss in detail the local stress relaxation associated with these two different kinds of hoppings. The local stress around the ellipsoid is obtained by summing over the stress on the ellipsoid and its nearest neighbors. The stress has six components and the stress autocorrelation function is given by $\langle \sigma_{ij}(0)\sigma_{ij}(t)\rangle$, where $i, j = x, y, z$. In the case of only Lennard-Jones fluid, $\sigma_{ij} = \sigma_{ji}$, but for particles interacting via GB and GB-LJ potentials, this is not so.

Figures 2(a) and 2(b) show the SAF around the first tagged ellipsoid, before and after the period it is hopping, respectively. Before the hopping, there is an anisotropy of the stress. The xy and yx components of the stress are much larger than the others, and also their correlations

cease to decay. *This anisotropy leads to a hopping of the ellipsoid, mostly in the z direction.* During the hopping, there is a relaxation of the SAF in xy and yx components, and after hopping all the components relax. Note that the total stress in all the components are also lower.

Figures 3(a) and 3(b) show the SAF around the second tagged ellipsoid, before and after the period it is hopping, respectively. Before the hopping there is an anisotropy of the stress. The yz and zy components of the stress are much larger than others, and also their correlations cease to decay. *This leads to the hopping of the ellipsoid, mostly in the x direction.* During and after the hopping there is an exchange of the stress. After the hopping, although the yz component of the stress relaxes and also the $t = 0$ value of all the components reduces, the SAF in the xz and zx components ceases to decay. Thus, this kind of motion in a ringlike tunnel does not lead to the relaxation of all the components of the stress.
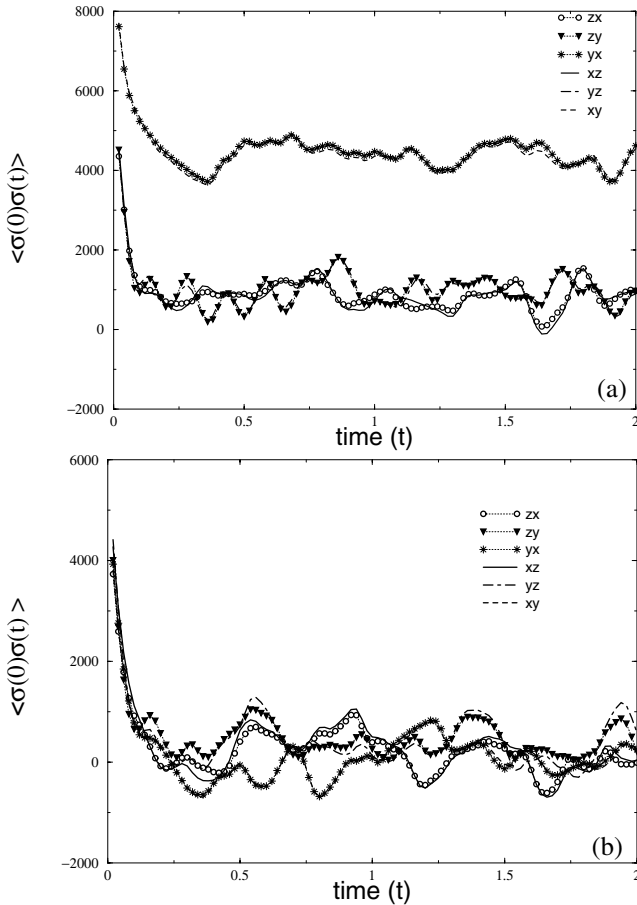

FIG. 2. (a) The different components of the local stress auto-correlation (obtained from the sum of the stress of the first ellipsoid and its nearest neighbors) function obtained before hopping, between $320\tau-330\tau$. (b) The same as (a) but the components of the SAF are obtained after hopping between $(340\tau-350\tau)$. The plots are at $P^* = 10$ and $T^* = 0.8$.
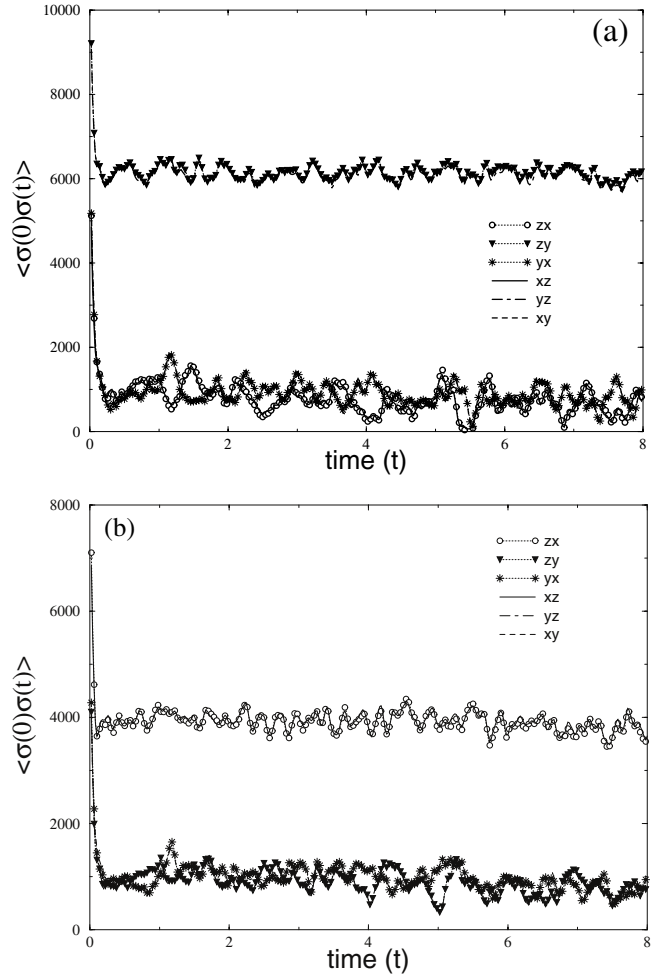

FIG. 3. (a) The different components of the local stress auto-correlation (obtained from the sum of the stress of the second ellipsoid and its nearest neighbors) function obtained before hopping, between $1590\tau-1630\tau$. (b) is the same as (a) but the components of the SAF are obtained after the hopping, between $1670\tau-1710\tau$. The plots are at $P^* = 10$ and $T^* = 0.8$.

The orientational correlation function of the first tagged particle relaxes more [inset of Fig. 1(a)] compared to that of the second tagged particle [inset of Fig. 1(b)] when computed in the respective intervals where they are hopping. From Figs. 2 and 3, we found that the local stress relaxation takes place when the first ellipsoid is hopping, whereas when the second ellipsoid is hopping, although there is an exchange of stress between its components, the local SAF does not completely relax. There is a direct connection between the local stress and the orientational relaxation functions, implying that rotation and viscosity are coupled even in a localized region.

In order to understand what happens to the surrounding of the local region when there is a relaxation of stress due to hopping, we have studied the stress autocorrelation function of a bigger region of 2σ around the first ellipsoid. We found there are about 62–67 particles in this region. Although there is an anisotropy of the components of the stress in this larger region, this anisotropy cannot be correlated with the direction of hopping. Some of the components of SAF build up immediately after hopping and in a later time it relaxes. Similar analysis when done in a even bigger region shows that it takes longer for the stress of that region to relax, and also the effect of the hopping is less.

In conclusion, we demonstrated that the *direction* of the hopping of the tagged particle is determined by the anisotropy in the stress. Anisotropic stress relaxation is different when there is a many-particle hopping and there is a motion in a ringlike tunnel. Although there is an exchange of stress between the components due to the particle motion, the stress relaxation is less in a ringlike motion. Interestingly, the effect of hopping is found to spread over the adjoining region like ripples with the amplitude decreasing with increasing distance from the ellipsoid. We note that in the case of the second tagged ellipsoid [Fig. 1(b)], although it translates more, the stress relaxation during its hopping is less—thus suggesting that translational motion and viscosity are decoupled even in a localized region. On the other hand, the orientational relaxation and also the stress relaxation is more for the first ellipsoid—thus suggesting that the orientational motion always remains coupled to viscosity. This is in agreement with the experimental results and, in fact, provides a microscopic explanation of the results which have been known for a long time. There can be an apparent connection between the stress tensor and the momentum circulation. Thus, it is possible that the nondecaying SAF implies that momentum circulation exists in a deeply supercooled liquid. Since the anisotropic stress contributes to the free energy of the system, a change in the anisotropy drives the system from one free energy minimum to the other.

When the anisotropy in the stress disappears and all the SAF relaxes, then the system definitely moves to a lower free energy minimum.

---

*Electronic address: bbagchi@sscu.iisc.ernet.in

[1] S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature (London) **393**, 554 (1998).
[2] C. A. Angell, Chem. Rev. **90**, 523 (1990); Luz-Maria Martinez and C. A. Angell (private communication).
[3] A. Mukherjee, S. Bhattacharyya, and B. Bagchi, J. Chem. Phys. **116**, 4577 (2001).
[4] L. Angelani, G. Parisi, G. Ruocco, and G. Viliani, Phys. Rev. Lett. **81**, 4648 (1998).
[5] C. D. Michele and D. Leporini, Phys. Rev. E **63**, 036701 (2001); **63**, 036702 (2001).
[6] G. Hinze, D. D. Brace, S. D. Gottke, and M. D. Fayer, Phys. Rev. Lett. **84**, 2437 (2000); J. Chem. Phys. **113**, 3723 (2000).
[7] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970); **55**, 4245 (1971).
[8] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13 200 (1996); M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **104**, 7210 (1996); **103**, 5684 (1995); G. Heuberger and H. Sillescu, J. Phys. Chem. **100**, 15 255 (1996).
[9] L. A. Deschenes and D. A. Vanden Bout, Science **292**, 255 (2001).
[10] C. K. Majumdar, Solid State Commun. **9**, 1087 (1971).
[11] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. **49**, 435 (1977); L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, New York, 1981).
[12] S. Sastry, Phys. Rev. Lett. **85**, 590 (2000); S. Sastry, Nature (London) **409**, 164 (2001).
[13] W. Kob and H. C. Andersen, Phys. Rev. E **51**, 4626 (1995); W. Kob and H. C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994).
[14] K. Vollmayr, W. Kob, and K. Binder, J. Chem. Phys. **105**, 4714 (1996); F. Sciortino, W. Kob, and P. Tartagila, Phys. Rev. Lett. **83**, 3214 (1999); B. Coluzzi, G. Parisi, and P. Verrocchio, J. Chem. Phys. **112**, 2933 (2000).
[15] H. C. Andersen *et al.,* Rapport d'activite scientifique du CECAM, pp. 82–1157 [7.4, 7.4.3].
[16] D. Brown and J. H. R. Clarke, Mol. Phys. **51**, 1243 (1984).
[17] J. M. Haile and H. W. Graben, J. Chem. Phys. **73**, 2412 (1980).
[18] J. G. Gay and B. J. Berne, J. Chem. Phys. **74**, 3316 (1981).
[19] S. Bhattacharyya and B. Bagchi, J. Chem. Phys. **115**, 9065 (2001).
[20] S. Bhattacharyya, A. Mukherjee, and B. Bagchi, J. Chem. Phys. (to be published).
[21] C. Bennemann, C. Donati, J. Baschnagel, and S. C. Glotzer, Nature (London) **399**, 246 (1999).